Integrated Atmospheric Deposition Network Implementation Plan

prepared by

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Introduction

The Great Lakes Water Quality Agreement, first signed in 1972, has evolved over the years. In 1987 new annexes were introduced into the 1978 version of the agreement. These updates to the agreement recognized the importance of the complete Great Lakes ecosystem. In particular, Annex 15 was included to deal with the problem of airborne contaminants in the Great Lakes Basin. The influence of airborne contaminants will be an important factor to consider when developing Lake-Wide Management Plans for each of the Great Lakes. Annex 15 has four main components: an enhancement of the measurement of the importance of the air pathway for toxic substances through the establishment of an integrated monitoring network; improvements in our understanding of the processes in the atmosphere that influence the fate of toxic substances through an enhanced research program; identification of the human health aspects of the problem; and the development of appropriate control strategies. The purpose of this document is to outline an implementation plan for the establishment jointly by Canada and the United States of the Integrated Atmospheric Deposition Network.

In July 1988, The International Joint Commission published the report to the Water Quality Board prepared by the Atmospheric Deposition Monitoring Task Force of the Surveillance Work Group. The report outlined a three-phase plan for addressing the problem of airborne toxic substances in the Great Lakes Basin. A key element of this plan was the establishment of an Integrated Atmospheric Deposition Network for the Great Lakes Basin. This network would consist of several Master (research grade) Stations augmented by a number of Satellite (routine) Stations. The objective of this network was to acquire sufficient, quality assured data to estimate with a specified degree of confidence the loading to the Great Lakes Basin of selected toxic substances. The relative importance of the atmospheric pathway could then be ascertained and appropriate control strategies developed. The IJC report also identified many critical research issues that must be addressed in order to understand and quantify the importance of the atmospheric pathway for toxic substances.

Although resources were scarce, some efforts to address the airborne toxics issues continued. A Canadian Master Station was established at Point Petre (1988) providing a platform for many agencies to take simultaneous measurements of a number of substances in a number of ways. The United States established a Master Station at Green Bay (1987) to monitor airborne toxics and study their effect on the region.

On December 4 to 5, 1989 a U.S./Canada group of managers and scientists met in Detroit to begin preparation of an implementation plan for the envisioned Integrated Atmospheric Deposition Network. The implementation provides detail and specific direction over the next six years and follows directly from the more general IJC report. Research issues were not explicitly addressed at the December meeting or in the document that follows, however, the importance of ongoing research in developing a clear understanding of atmospheric pathways and fate of toxic substances should not be understated.

The following document considers various aspects of a workable implementation plan. The problem was divided into three parts: (1) the choice of chemicals to be measured, (2) the siting criteria and sampling methodology, and (3) the Quality Assurance/Quality Control required. These categories are somewhat arbitrary and the inter-relationships among them are many. However, for planning purposes it is useful to maintain the distinction.

Determination of Chemicals to be Measured

Several hundred toxic chemicals have been detected in the Great Lakes Basin of which many are thought to have a significant airborne component. In choosing appropriate chemicals to measure in the Integrated Atmospheric Deposition Network a number of criteria are important.

Criteria for Selection of Target Atmospheric Pollutants

- The substances are listed in List 1 of Annex 1 of the Great Lakes Water Quality Agreement. This list includes substances believed to be toxic and believed to be present in the Great Lakes.

- The substance is currently an established or perceived water quality problem. The toxicology of the substance may indicate a potential serious problem; the substance may bio-accumulate or be persistent. The loading to the ecosystem can then become significant. The human health concerns could be a factor.

- The substance is now on the Water Quality Board's list of critical pollutants.

- Evidence exists that the chemical is present in the atmosphere (rain, snow, aerosol) and/or has an important atmospheric pathway (volatilization; occurrence in remote lake/peat sediments).

- The chemical should be feasible to measure in a routine monitoring network. Routine in this sense means a sequence of collection, transport, processing and analysis procedures can be performed in a prescribed manner.

The Selection of Phase I Substances

Phase I is considered to be the first two years of the program. Naturally in this phase a significant emphasis will be on research. Evidence is required to establish whether any toxic chemical can be routinely monitored in ambient air or in wet deposition samples. The dry deposition will be estimated using air concentrations. Therefore, the toxic chemicals measured in Phase I should be selected to demonstrate feasibility and efficacy of the methodology, namely:

1. PCBs: Total PCBs and major congeners
2. HCHs: α, γ isomers
3. PAHs: B[a]P (goal)[1]
4. Pb

The selection of specific compounds within families will be established by regular consultation.

As a second priority, methodologies will be developed and applied for the following compounds:

- Cl-pesticides such as DDT plus metabolites; chlordane; nonachlor; heptachlorepoxide; methoxychlor; dieldrin; HCB; endrin

- Trace Metals - Arsenic, Selenium, Cadmium, Mercury

Substances Requiring Extensive Methodology Development

A number of other chemicals are known or suspected of having an important atmospheric pathway. However, the following chemicals require extensive method development and/or confirmation of their importance. The topics requiring attention include:

- Some chemicals, such as the Cl-benzenes, with an established atmospheric component to their environmental cycling, may require methodology development in order to take valid measurements.

- A wide range of PAHs are present in the Great Lakes ecosystem. Although there are currently very few measurements, PAHs have an important atmospheric pathway. The measurement methodology for a broad range of PAHs requires considerable improvement.

- Toxaphene is present in the Great Lakes ecosystem and has been shown to be transported by air from large distances. The analytical methodology requires considerable improvement before extensive atmospheric sampling can be done.

- There are a variety of toxic substances which may have an atmospheric pathway but as yet there is a lack of definitive data to establish the existence or importance of this pathway. As

[1] The PAH B[a]P is among the most difficult of all the PAHs to determine. Sampling is particularly difficult as this PAH is chemically very reactive with ambient oxidants and is subject to UV degradation. Other less reactive PAHs will be sampled along with B[a]P. There is no doubt that B[a]P is an important substance and work should continue on an appropriate sampling procedure.

well, routine analytical procedures generally do not exist for these substances. For example, co-planar PCBs, dioxins and furans.

- New chemicals are being introduced each year into the Great Lakes Basin. The significance of these chemicals is largely unknown. A range of modern agrochemicals, such as Triazines, Alachlor/Metachlor, as well as, industrial chemicals such as plasticizers, PCB substitutes, etc. may have to be studied.

Stations, Siting, Samplers, and Sampling Protocols

Each of the three phases of the Integrated Atmospheric Deposition Network Plan will last for a period of two years, commencing with the implementation date of January 1990. This section considers four aspects of the implementation:

- The number of stations in the network
- The siting criteria for those stations
- The sampling equipment to be used at those stations
- The sampling protocol for the acquisition of deposition data

Number of Stations in the Network

The final design of the network will be based on the knowledge gained during the phased approach of the implementation. As such, the final number of stations is still open to determination based on criteria associated with spatial homogeneity of the deposition fields, temporal scales of the deposition variation, and the importance of local physical variables of deposition, many of which can be identified but currently are not quantified. The first priority of the network will be to determine the deposition of toxic chemicals to the Great Lakes from the air in terms of annual averages, but to the extent possible, the network will address source region attribution questions. While the deposition processes are governed by very short time scales, annual average deposition can be determined with much longer scale sampling times. Although sampling should occur at the shortest temporal scale which can be accommodated by data quality, logistics and cost, the smallest scales will be below network resolution. It is felt that the design of the IJC Plan is basically correct for the objective of determining longer scale loadings to the Great Lakes Basin; that is, there is a requirement for five research grade Master Stations throughout the Great Lakes Basin and up to twenty-two routine measurement or satellite stations within the basin.

During Phase I of the Plan, the Parties will initiate sampling at one Master Station site each. Master Stations will be designed with sufficient space and infrastructure to accommodate temporary, intensive research efforts. Canada has chosen Point Petre on Lake Ontario as its initial

Master Station site. The U.S. has operated a Master Station grade site at Green Bay from April 1987 to the present. It is planned that during Phase I, a more regionally representative site will be established on the south shore of Lake Superior during the summer of 1990. The Green Bay site will continue to operate at least until the end of the Green Bay Mass Balance Study.

By April 1991, Canada will initiate construction of the third Master Station on Lake Huron. Two U.S. Master Stations will be sited: one on the southeastern shore of Lake Erie and one on Lake Michigan. The Lake Erie site will be implemented at the beginning of Phase II and the Lake Michigan site during Phase II. Phase II under this plan will be initiated in January 1992 and will run through December 1993. During 1992, five satellite stations in Canada and six satellite sites in the U.S. will be chosen and implemented. The intent is that one satellite station will be added to each side of each of the four international lakes, two U.S. stations to Lake Michigan and one Canadian station northwest of the Great Lakes Basin.

Analysis of data from the five Master Stations and eleven satellite sites for Phases I and II will be completed by June 1994. At that time the Parties will determine the need for, and the necessary sites for, up to an additional eleven satellite stations. The intent is to have one station added on each side of each international lake, two U.S. stations on Lake Michigan and an additional station northeast of the Great Lakes Basin in Canada.

Siting Criteria

It is desirable to place each station physically as close to the Lakes as is logistically possible. Although the impact of urban sources on deposition to the lakes and of land/lake breeze circulation was considered, these effects will be difficult to discern, in a statistical sense, from the general noise in the annual average deposition data and thus should be ignored initially. Research to quantify the level of the smaller scale impacts must take place within Phases I and II. To this end, use of a ship or offshore platform for collection of samples downwind of urban centres is recommended as an effective research approach especially when coupled with model studies.

A siting criteria document will be produced by May 1990. The document will consider the general principles of future station siting and give optimal guidelines to be followed by the Parties. When no appropriate site can be found meeting all criteria, it is agreed that the Parties may deviate from the guidelines, provided there is reasonable justification and mutual consultation.

Sampling Equipment

There are currently variations in the types of samplers being used to measure air and precipitation concentrations of organics and trace metals in the Great Lakes. It is not recommended at this time that a formal decision be taken on the types of samplers to be used in the network but rather that Phase I be used to evaluate the sampler methodologies used by the agencies involved in Great Lakes sampling. To that extent, reference is made to Tables 4 and 5 of the IJC plan. The initial Master Station complement will consist of:

- one (1) precipitation sampler to measure nutrients and inorganic chemicals in wet deposition in order to compare with existing networks
- one (1) precipitation sampler to measure trace metals in wet deposition
- replicated precipitation samplers to measure toxic organics in wet deposition (two or more)
- replicated high-volume air samplers with filter/adsorbent combinations to measure gaseous and particulate toxic organics in air (two or more)
- one (1) high-volume sampler to measure total suspended particulate mass loading in air and total organic carbon
- one (1) sampler for trace metals in air
- a set of meteorological instruments to measure rain and snow intensity and amount, temperature, relative humidity, wind velocity, and solar radiation
- dichotomous Hi-Vol samplers[2]

The initial satellite stations will have one sampler for the measurement of each of:

- trace metals in precipitation
- trace metals in air
- toxic organics in precipitation
- toxic organics in air
- total suspended particles

plus meteorological instruments to measure rain and snow intensity and amount, temperature, relative humidity, and wind velocity.

[2] High-volume and low-volume dichotomous air samplers will be installed at a single Master Station early in Phase I in order to evaluate their performance side-by-side with existing air samplers. Before the beginning of Phase II, a decision will be made on whether dichotomous samplers will be chosen for air sampling at all Master sites and Satellite sites.

During Phase I, differing sampling methodologies will be examined and not precluded between the Parties. The QA/QC programme will address the significance of the difference between the sampling methodologies. Subsequently, after the Critical Network Design Review (June 1992), the Coordinating Committee will make recommendations to the Parties for sampling methodologies for the Master and Satellite Stations.

Sampling Protocols/Analysis Protocols

It is recognized that current sampling and analysis protocols differ between the Parties due to a number of factors including sample-handling capacity, sampling protocols which agree with other sampling networks, expected need for valid sample volumes, and tested sampling procedures. During Phase I such disagreements between protocols will be accepted but comparability should be established by the time of the Critical Network Design Review during Phase II (June 1992). Each agency will document their current sampling and analysis protocols for exchange under the QA/QC programme before June 1990.

It is recognized that the requirement of the network to deliver estimates, with a specified degree of confidence, of annual deposition to the Great Lakes is not necessarily the same requirement as to deliver information on source identification information for input to remedial action strategies. Source identification information can be delivered by specific research programmes in cooperation between the Parties for intensive periods at the Master Stations or other appropriate sites.

Quality Assurance and Quality Control

The Integrated Atmospheric Deposition Network will consist of individual stations, run by different U.S. and Canadian agencies. To be useful, the data generated by each of the agencies will need to be combined into one data set. Thus the data from each individual project will need to be demonstrated to be of comparable quality. Generation of comparable data by the individual agencies will only be accomplished if each of the agencies adheres to a thorough, Program-wide QA/QC Plan.

The work will begin immediately on the design and development of a Quality Assurance Program Plan for the overall monitoring network. This plan will address the following issues:

- Quality assurance objectives
- Procedures for demonstrating and assessing perfomance

Quality Assurance Objectives

A clear definition will be provided of relevant QA components, which will be used to assess the performance of a monitoring agency, and ultimately determine the acceptance/non-acceptance of a data set.

It is agreed that clear data quality objectives be set for each chemical (or group of chemicals) to be monitored on a routine or research basis. For each contaminant, these objectives will be based upon the estimated amount entering the Great Lakes and the significance of the atmospheric components.

The data quality objectives will govern all aspects of the measurement process, i.e. sampling, analysis, data reduction/reporting. The data quality objectives will be used as the basis for the final acceptance of data from a given agency.

It will be the responsibility of each agency to document compliance/attainment of the data quality objectives. The program plan will also provide clear guidelines as to the procedures by which this attainment should be assessed.

Procedures For Demonstrating and Assessing Performance

For each of the specified quality assurance components included in the data quality objectives, procedures will be defined for individual agencies to demonstrate attainment. For instance, precision of analysis for a given target species should be assessed by the approaches of duplicate sampling in the field. Replicate analyses in the laboratory will provide another measure of precision.

The procedures can be roughly divided into:

- Internal procedures
- External procedures

Internal procedures can be defined as those methods that can be employed by a given agency to confirm data quality, e.g. regular calibrations, complete documentation, internal audits.

External procedures are defined as those methods which will require intervention by an outside party, e.g. external audits, laboratory inter-comparisons, co-location of samplers employing different approaches, etc.

Preparation of the Plan

The QA Program Plan will be developed by October 1990. Development of the network QA Program will be undertaken by a contractor under the management of the QA/QC Working Group. To assist in the development of the Program Plan, each agency will provide copies of existing approved QA Project Plans to the co-chairs of the QA/QC Working Group by the end of May 1990.

Implementation of the Plan

To ensure the effective implementation of the QA Plan, the following actions are required.

- The appointment of a QA Manager to oversee the whole program is strongly recommended. Failing that, the appointment of QA officers by each of the parties will be required.

- To assure compliance with the QA/QC Program Plan and to demonstrate the production of comparable data, the QA Manager will be responsible for the organization and execution of external performance evaluation studies. This aspect needs to be implemented as soon as possible, since a considerable amount of data has already been collected by the various groups involved. The QA Manager will coordinate a series of sample exchanges/intercomparison studies during early 1991 (or earlier if feasible).

- Individual Agencies will be required to demonstrate compliance with the data quality objectives in the QA Plan by October 1991. The supporting documentation that must be submitted to the QA Manager at that time will include:

    - QA Project Plans
    - QA Manuals
    - Performance Assessment Results

- At this point, the QA Manager will decide upon the overall suitability of data being generated by a given agency.

- The QA Manager will have ultimate responsibility for acceptance of final data sets from approved agency monitoring networks.

Summary of Key Milestones

PHASE I	PHASE II	PHASE III
January 1990*	January 1992	January 1994

- QA/QC
  - Exchange QA Project Plans (May/90)
  - Coordinate Agency QA Plans (e.g. Intercomparison/Round Robin) (1990)
  - Contract IADN QA Manager
  - Develop IADN Program Plan (October/90)
- Siting Criteria (May/90)
- Select/construct Master Sites (1990)
  - Pt. Petre (CAN; Lake Ontario)
  - Keweenau Peninsula (U.S.; Lake Superior)
- Co-location of CAN/U.S. sampling equipment (1990), Pt. Petre
- Select chemicals for monitoring (Jan./90)
- Meeting CAN/U.S. Coordinating Committee (2 x per year)
- Initiate research activities
- Select/construct CAN Master Site (April/91) (Lake Huron)
	- Update estimates of atmospheric deposition (Jan./92 thereafter annually; CAN/U.S. Coord. Comm.)
	- Review IADN and research activities (Jan./92; CAN/U.S. Coord. Comm.)
	- Project compliance with IADN Program Plan (QA) (IADN QA Manager)
	- Review and modify chemical list for IADN
	- Select/construct U.S. Master Site(s)
	  - Lake Erie site (May/92)
	  - Lake Michigan (east side) (May/93)
	- Select/construct Satellite Stations (1992)
	  - 1 per international lake (U.S.)
	  - 1 per international lake (CAN)
	  - 2 sites on Lake Michigan (U.S.)
	  - 1 site upwind of GL's (ELA) (CAN)
	- Continue research activities
		- Update estimates of atmospheric deposition (Jan./94; annually; CAN/U.S. Coord. Comm.)
		- Review IADN and research activities (Jan./94; CAN/U.S. Coord. Comm.)
		- Review/modify chemical list
		- Select/construct Satellite Stations; number and locations to be determined
		- Continue research activities
		- Network Implementation (Dec./95)

* each phase is 2 years in length